# PERMIT APPLICATION INSTRUCTIONS FOR MUNICIPAL SURFACE WATER EFFLUENT MONITORING REQUIREMENTS

All municipal permittees discharging to surface waters and applying for a permit reissuance must monitor the physical, chemical and biological characteristics of each outfall. The monitoring that each permittee must perform is based on the category of discharger (major or minor) and also on individual circumstances. Results of monitoring must be reported on Forms A-1 through A-3 of the application form.

These instructions are provided to help you complete Forms A-1 through A-3. To help avoid problems, we suggest that you forward a copy of these instructions and any information on what calculated limits for any of the substances would be (if you know) to your laboratory.

## ➢ What are my testing requirements?

You must complete one Effluent Monitoring Form (Form A-1) for each outfall that discharges effluent to surface waters. Analyze at lease one sample for each line on the form. If you analyze additional samples, report results on the Additional Monitoring Form (Form A-2). Other general instructions are:

- **Discharge Monitoring Report Data** - If your current permit requires regular monitoring and reporting of any parameter for which this application requires testing, you need not retest the parameter nor resubmit the test results on Form A-1 (see the Discharge Monitoring Report Information section of the instructions for more information).
- **Past Monitoring Results** - Any monitoring results collected within the last 5 years may be used toward the monitoring required by the application if the monitoring results are representative of the current discharge.
- **Identical Outfalls** - If you have two or more outfalls that discharge substantially identical wastewaters, you may request permission from the Department to sample and analyze only one of the outfalls. If your request is granted, on a separate sheet of paper attached to the completed application, identify which outfall you did test, and describe why the outfalls that you did not test are substantially identical to the outfall that you did test.

## ➢ How must I perform this testing?

It is important that you provide the Department with quality monitoring data, since that data will be used to help determine what regulatory requirements we place in your reissued permit. The three important steps in the process of providing the data are sampling, laboratory testing and data reporting. (For more detailed guidance on steps to follow to accomplish the required monitoring, see the Monitoring Procedures Guidance, which is included as an attachment to these instructions.)

- **Sampling** - Data generated by your laboratory are only as good as the samples you collect. You must insure that the composition of your samples is as close as possible to the composition of the wastewater streams you are sampling. To do this you must consider sample time and location and you must minimize contamination. The time when you

sample should be representative of your normal operation, to the extent feasible, with all processes which contribute wastewater in normal operation, and with your treatment system operating properly with no system upsets. Sample types, preservation methods and maximum holding times are listed in Table 1, attached to these instructions. Although Table 1 specifies 24-hour composite samples for many of the substances, the Department may waive composite sampling for any outfall for which you demonstrate that use of an automatic sampler is not feasible and that a minimum of four grab samples will be representative of the discharge from the outfall. Sample preservation must be performed immediately. Labs will need to check if samples arrived at the laboratory meeting temperature requirements.

If you are required to monitor for a parameter more than once, you must ensure a sufficient interval between discharge samples. If we have not specified a monitoring interval for a parameter, weekly intervals are generally about right. Please do not sample more frequently than once every 3 days unless we so direct you.

- **Laboratory Testing** - Sample analyses shall be performed by laboratories that are certified by the Department. You may contact the Laboratory Certification Program, WI DNR, 101 S. Webster St., Box 7921, Madison WI 53707, (608) 267-7633 for a current list of certified labs. Alternatively, visit the Program's World Wide Web Site at http://www.dnr.state.wi.us/org/es/science/lc/search/. Select a lab that can meet your needs for proper sensitivity and data quality.

  We suggest that you provide a copy of the Effluent Monitoring Form, along with these instructions, to your laboratory. The Effluent Monitoring Form will tell your laboratory personned what substances they need to test and the quality control information they need to supply with the data.

  Unless instructed otherwise, you must use approved analytical test methods as identified in ch. NR 219, Wisconsin Administrative Code. For many pollutants, more than one analytical test method is approved. Your lab should pay close attention to analytical detection limits in selecting the proper test methods and should use any available information that might help predict effluent limitations to guide them in this effort. Recognize that detection limits can be affected by analytical test methods and clean up procedures, interference or sample contamination.

  The Department has listed recommended test methods in **Table 1** (attached to these instructions) in an attempt to balance the need to measure compounds below levels that are environmentally significant against method sensitivity and positive compound identification. A number of the substances given in Table 1 are toxic in the environment at levels below the analytical detection limits of even the most sensitive analytical methods. If you report these substances as not detected and your lab did not use a method as sensitive as the one recommended in Table 1 or reports an unusually high detection limit above the Department's level of concern, the Department may require you to repeat the testing. However, you may be able to provide an explanation for the high detection limit and indicate those steps taken by your laboratory to lower the detection limit.

- **Data Reporting** - You must report the data on the Effluent Monitoring Form.

  A numerical test result, by itself, is not very meaningful. The other information you report on the Effluent Monitoring Form will be used to help determine how accurately the data represents your discharge. It should also serve as a quality check for you. If you find that an unusual circumstance or qualifying information pertains to a certain piece of data, you should immediately take steps to clarify the situation, such as through re- sampling.

  At your request, the Department can supply you with electronic copies of the Effluent Monitoring Form. It may make it easier for you to display the data. The Department has made electronic copies of the report form available to many commercial laboratories. Therefore, your contract lab may be able to produce a computer- generated analytical report identical to this form. In that case you may simply attach a copy of the lab's analytical report and save yourself the need to transcribe the data onto this paper form. We still recommend that you supply a copy of the Effluent Monitoring Form (along with any preliminary limits if included in the application package) to your laboratory so they can provide you the most complete information.

➢ **Effluent Monitoring Form (Table A-1)**

- **Blank Cells** - Please fill in all blank cells in the table. Where the cells have been pre-filled or shaded, you need not record any further information. You may use ditto marks or simply draw a vertical arrow down a column for entries, which are the same on consecutive lines.

- **Outfall Number** - Please make sure the correct outfall number appears on each page of the form.

- **Parameters** - You must monitor for each parameter in the table. The table is pre-printed with the parameters you must test and, when multiple samples are required, it contains the correct number of lines for the test results (i.e., one line for each required test result).

- **Additional Sample Results** - You may provide more sample results than specified by the table. For example, if your initial sample result for a substance is greater than 1/5 of your expected effluent limitation, or if you have some reason to think that the data you have is not representative of your discharge, you probably will want to sample at least several more times. To report that additional data, use the Additional Monitoring Form by filling in as many lines as there are sample results. If you need more lines than are on the sheet, please make photocopies of the blank form before you start.

- **Properly Collected and Representative Effluent Samples** - Indicate whether or not the effluent sample was properly preserved and handled and is representative of normal operating conditions. If not, the effluent must be re-sampled.

- The information necessary to complete the form should be available to you on the

analytical report(s) provided to you by your contract laboratory. Sometimes the Department finds it necessary to refer directly to the lab reports. Please attach copies of lab report for any monitoring not done to fulfill routine, permit-required effluent discharge monitoring.

**Column by Column Instructions for Table A-1**

- **Parameter Code** - This is a unique number that normally will be pre-printed and is used as a reference by the Department.

- **Parameter Name** - The parameter name column will normally be pre-printed with the name of the substance for which you must report data. The CAS (Chemical Abstract Services) number for that parameter is also pre-printed on the form.

- **Sample Result** - Record the numerical result as provided to you by your laboratory. Make sure to report the correct results for the units reported. If a substance is not detected in a sample, report the result as < (less than) the value of the detection limit. For example, if the substance ammonia nitrogen is not detected and your laboratory indicates that the detection limit is 0.1 mg/L, report the result as <0.1 in the sample result cell.

- **QC Flags** - Use this column to signal that there has been some sort of laboratory quality control (QC) exceedance. The entry in this space should normally be a letter of the alphabet or some other common typographical symbol. Similar to how a footnote is used in text documents, explain the meaning of the "flag" at the bottom of the report form.

  *(NOTE: Flagged data are not necessarily bad data. However, unless your laboratory has documentation, which shows that a quality control exceedance did not affect sample results, please arrange for re-analysis or re-sampling and analysis for affected parameters.)*

- **Units** - The units column normally will be pre-printed with the units of measurement in which you should report the analytical results. If your laboratory reports results for a given substance in different units, you will need to convert them to the pre-printed units. Usually, a change in units requires that you move the decimal point 3 places to the right or left. For example, 0.018 mg/L is the same as 18 μg/L. 8 ng/L is the same as 0.008 μg/L. If you are unsure how to convert the results into the required units, contact the permit drafter who is identified in the cover letter that accompanied this application package.

- **Detection Limit (LOD)** - Record a numerical value for the limit of detection (LOD) reported to you by your laboratory. Sometimes this quantity is called to the method detection limit (MDL). You need not report a detection limit for certain substances (the space will be shaded) such as for temperature or pH.

- **LOQ (Limit of Quantitation)** - Record the numerical value for the limit of quantitation (LOQ) reported to you by your laboratory. You need not report a limit of quantitation for certain substances, such as temperature or pH.

- **Analytical Method** - Record what laboratory analytical method was used to test for the substance. Usually, methods are specified using method numbers. Refer to Table 1 of these instructions for a listing of recommended analytical test methods.

- **Confirmed Organics (Y/N)** - For organic substances, **if you report a detected result**, indicate if a detected result has been confirmed. GC/MS methods do not require separate confirmation. If a GC/MS method was used to generate a detected result, enter Y (yes) in this column. If a GC method produced a detect, answer Y if the detect was confirmed and N (no) if it was not. You may need to consult with your laboratory if this information is not provided on the laboratory's report of analytical results.

- **Sample Collection Date** - Record the day, month and year (mm/dd/yy) when the sample was collected. If the sample is a 24-hour composite, please show the end date of the compositing period.

- **Extraction Date** - For organic substances, record the day, month and year (mm/dd/yy) when the sample was extracted in the laboratory.

- **Analysis Date** - Record the day, month and year (mm/dd/yy) when the sample was analyzed in the laboratory or in the field.

- **Lab ID Number** - Provide the nine-digit Wisconsin laboratory certification number of the lab that performed the analyses. If analytical testing was sub-contracted to another lab, you still must provide the certification number of the lab that performed the analyses.

- **Sample Type (Co/Gr)** - Record the type of sampling used for that parameter. ("Co" means 24-hour composite sample. "Gr" means grab sample.) Table 1 of these instructions lists required sample types by parameter.

- **DMR (Discharge Monitoring Report)** - You do not have to retest those parameters that your WPDES discharge permit currently requires you to monitor, nor do you have to resubmit the monitoring data. Simply place a check mark in the DMR column for those parameters.

- **Additional Monitoring Form (Table A-2)**

  Reporting Additional Monitoring Results - If you have sampled for a parameter more frequently than that required by the Effluent Monitoring Form, please provide the extra test results on the Additional Monitoring Form. Copy the correct parameter code, name and units from the Effluent Monitoring Form and write this information in the correct columns on the Additional Monitoring Form. Use as many lines as there are results.

  The general instructions and column instructions are the same as for the Effluent Monitoring Form.

- **Discharge Monitoring Report (DMR) Information (Table A-3)**

  When evaluating effluent quality, the Department usually assumes that the information reported by the permittee on their Discharge Monitoring Reports (DMR), Forms 3200-28 or 3200-40, for the last 36 months is representative of the permittee's current discharge.

  If you agree that the last 36 months of DMR information accurately represents the current discharge from your outfall, place a check mark in the first box.

  If you believe that a time period other than the last 36 months is representative of the current discharge, check the second box, specify the time period over which you believe DMR data are representative of the current discharge and provide the reasons for your belief. For example, a time period less than 36 months would be appropriate if 18 months ago a contributing industry added or modified a significant production process or a wastewater treatment process.

  If you believe certain DMR data points over the selected time period are not representative of the current discharge, check the third box, identify the data points and provide the reasons for your belief.

# ADDITIONAL INFORMATION

## TABLE 1. - SAMPLING, PRESERVATION AND ANALYTICAL INFORMATION

### Substances Which May Require Testing With Permit Applications

| Parameter | Sample Type[a] | Recommended Analytical Test Methods[b] | Preservation[c] | Maximum Holding Time[c] |
|---|---|---|---|---|
| COMMON POLLUTANTS | | | | |
| Biochemical Oxygen Demand ($BOD_5$) | 24-hr. comp. | - | Cool to $4^0C$ | 48 hours |
| Chemical Oxygen Demand (COD) | 24-hr. comp. | - | Cool to $4^0C$ | 28 days |
| Chlorides, Total | 24-hr. comp. | - | None requir EPA 335.4ed | 28 days |
| Chlorine, Total Residual | Grab | EPA 330.2 (amperometric), 330.5, or electrode | Analyze immediately | - |
| Nitrogen, Ammonia | 24-hr. comp. | - | Cool to $4^0C$, $H_2SO_4$ to pH < 2 | 28 days |
| Oil and Grease | Grab | EPA 1664 | Cool to $4^0C$, pH to < 2 | 28 days |
| PH | Grab | - | Analyze immediately | - |
| Phosphorus, Total | 24-hr. comp. | - | Cool to $4^0C$, $H_2SO_4$ to pH < 2 | 28 days |
| Suspended Solids, Total | 24-hr. comp. | - | Cool to $4^0C$ | 7 days |
| Temperature | Grab | - | Analyze in field | - |
| METALS, CYANIDE HARDNESS AND PHENOLS | | | | |
| Antimony, Total Recoverable | 24-hr. comp. | EPA 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Arsenic, Total Recoverable | 24-hr. comp. | EPA 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Beryllium, Total Recoverable | 24-hr. comp. | EPA 200.7 or 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Cadmium, Total Recoverable | 24-hr. comp. | EPA 200.7 or 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Chromium, Hexavalent | Grab | EPA 218.6 | Cool to $4^oC$ | 24 hours |
| Chromium, Total Recoverable | 24-hr. comp. | EPA 200.7 or 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Copper, Total Recoverable | 24-hr. comp. | EPA 200.7 or 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Cyanide, Total | Grab | EPA 335.4 | Cool to $4^oC$, NaOH to pH > 12,neutralize $Cl_2$ | 14 days |
| Cyanide, Amenable | Grab | EPA 335.1 | Cool to $4^oC$, NaOH to pH > 12,neutralize $Cl_2$ | 14 days |
| Lead, Total Recoverable | 24-hr. comp. | EPA 200.7 or 200.9[d] | $HNO_3$ to pH < 2 | 6 months |
| Mercury, Total Recoverable | Grab[e] | EPA 1631[d] | $HNO_3$ to pH < 2 | 28 days |
| Nickel, Total Recoverable | 24-hr. comp. | EPA 200.7 or 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Selenium, Total Recoverable | 24-hr. comp. | EPA 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Silver, Total Recoverable | 24-hr. comp. | EPA 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Thallium, Total Recoverable | 24-hr. comp. | EPA 200.7 or 200.9 [d] | $HNO_3$ to pH < 2 | 6 months |
| Zinc, Total Recoverable | 24-hr. comp. | SW-846 7950 or EPA 200.7 | $HNO_3$ to pH < 2 | 6 months |
| Hardness (Total as $CaCO_3$) | 24-hr. comp. | - | $HNO_3$ to pH < 2 | 6 months |
| Phenols, Total | 24-hr. comp. | - | Cool to $4^oC$, $H_2SO_4$ to pH < 2 | 28 days |
| VOLATILE ORGANICS | | | | |
| Acrolein | Grab | SW-846 8260B | Cool to $4^oC$, neutralize $Cl_2$, adj. pH to 4-5 | 14 days |
| Acrylonitrile | Grab | SW-846 8260B | Cool to $4^oC$, neutralize $Cl_2$ | 14 days |
| Benzene | Grab | SW-846 8260B | Cool to $4^oC$, neutralize $Cl_2$, HCl to pH < 2 | 14 days |
| Bromodichloromethane (dichlorobromo-methane) | Grab | SW-846 8260B | Cool to $4^oC$, neutralize $Cl_2$ | 14 days |

| Parameter | Sample Type[a] | Recommended Analytical Test Methods[b] | Preservation[c] | Maximum Holding Time[c] |
|---|---|---|---|---|
| Bromoform | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Carbon tetrachloride | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Chlorobenzene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$, HCl to pH < 2 | 14 days |
| Chlorodibromo-methane (dibromochloromethane) | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Chloroethane | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Chloroform | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Chloromethane (methyl chloride) | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| 1,2-Dichlorobenzene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$, HCl to pH < 2 | 14 days |
| 1,3-Dichlorobenzene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$, HCl to pH <2 | 14 days |
| 1,4-Dichlorobenzene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$, HCl to pH <2 | 14 days |
| 1,1-Dichloroethane | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| 1,2-Dichloroethane | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| 1,1-Dichloroethylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| *cis*-1,2 Dichloroethylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| *Trans*-1,2-Dichloroethylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| 1,2-Dichloropropane | Grab | SW-846 8260B | Cool to 4°C,neutralize $Cl_2$ | 14 days |
| 1,3-Dichloropropane | Grab | SW-846 8260B | Cool to 4°C,neutralize $Cl_2$ | 14 days |
| 1,1-Dichloropropylene | Grab | SW-846 8260B | Cool to 4°C,neutralize $Cl_2$ | 14 days |
| *cis*-1,3-Dichloropropylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| *Trans*-1,3-Dichloropropylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| 2,3-Dichloropropylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Ethylbenzene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$, HCl to pH < 2 | 14 days |
| Methyl bromide (bromomethane) | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Methylene chloride (dichloromethane) | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| 1,1,2,2-Tetrachloroethane | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Tetrachloroethylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Toluene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$, HCl to pH < 2 | 14 days |
| 1,1,1-Trichloroethane | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| 1,1,2-Trichloroethane | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Trichloroethylene | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| Vinyl Chloride | Grab | SW-846 8260B | Cool to 4°C, neutralize $Cl_2$ | 14 days |
| ACID EXTRACTABLE COMPOUNDS (Phenols) | | | | |
| 2-Chlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 3-Chlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 4-Chlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,3-Dichlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,4-Dichlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,5-Dichlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |

| Parameter | Sample Type[a] | Recommended Analytical Test Methods[b] | Preservation[C] | Maximum Holding Time[C] |
|---|---|---|---|---|
| 2,6-Dichlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 3,4-Dichlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,4-Dimethylphenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,3-Dinitrophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,4-Dinitrophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,5-Dinitrophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2-Methyl-4-chlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 3-Methyl-4-chlorophenol (*para*-chloro-*meta*--cresol) | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 3-Methyl-6-chlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2-Methyl-4,6-dinitrophenol (4,6-dinitro-*ortho*-cresol) | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2-Nitrophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 4-Nitrophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Pentachlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Phenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,3,4,6-Tetrachlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,4,5-Trichlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 2,4,6-Trichlorophenol | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| BASE/NEUTRAL COMPOUNDS | | | | |
| Acenaphthene | 24-hr. comp. | SW-846 8270C or 8310 | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Acenaphthylene | 24-hr. comp. | SW-846 8270C or 8310 | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Benzidine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Bis(2-chloroethoxy) methane | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Bis(2-chloroethyl) ether | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Bis(2-chloroisopropyl) ether | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Bis(2-ethylhexyl) phthalate | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| 4-Bromophenyl-phenyl ether | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Butyl benzyl phthalate | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| 2-Chloronaphthalene | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| 4-Chlorophenyl-phenyl ether | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| 3,3'-Dichlorobenzidine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |
| Diethyl phthalate | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| Dimethyl phthalate | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| Di-*n*-butyl phthalate | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| 2,4-Dinitrotoluene | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| 2,6-Dinitrotoluene | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Di-*n*-octyl phthalate | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| 1,2-Diphenylhydrazine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Hexachloroethane | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| Isophorone | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| N-Nitrosodi-*n*-butylamine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |

| Parameter | Sample Type[a] | Recommended Analytical Test Methods[b] | Preservation[c] | Maximum Holding Time[c] |
|---|---|---|---|---|
| N-Nitrosodiethylamine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| N-Nitrosodimethylamine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| N-Nitrosodiphenylamine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| N-Nitrosodi-*n*-propylamine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| N-Nitrosopyrrolidine | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Naphthalene | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Nitrobenzene | 24-hr. comp. | SW-846 8270C | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| 1,2,4-Trichlorobenzene | 24-hr. comp. | SW-846 8270C | Cool to 4°C | 7 days[f] |
| Chlorinated Hydrocarbons Requiring Specialized Testing | | | | |
| Hexachlorobenzene | 24-hr. comp. | SW-846 8121 (GC) | Cool to 4°C | 7 days[f] |
| Hexachlorobutadiene | 24-hr. comp. | SW-846 8121 (GC) | Cool to 4°C | 7 days[f] |
| Hexachlorocyclopentadiene | 24-hr. comp. | SW-846 8121 (GC) | Cool to 4°C | 7 days[f] |
| Pentachlorobenzene | 24-hr. comp. | SW-846 8121 (GC) | Cool to 4°C | 7 days |
| 1,2,4,5-Tetrachlorobenzene | 24-hr. comp. | SW-846 8121 (GC) | Cool to 4°C | 7 days[f] |
| Polynuclear Aromatic Hydrocarbons Requiring Specialized Testing | | | | |
| Anthracene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Benzo(*a*)anthracene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Benzo(*a*)pyrene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Benzo(*b*)fluoranthene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Benzo(*ghi*)perylene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Benzo(*k*)fluoranthene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Chrysene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Dibenzo(*a*,*h*)anthracene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Fluoranthene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Fluorene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Indeno(*1,2,3-cd*)pyrene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| Phenanthrene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days |
| Pyrene | 24-hr. comp. | SW-846 8310 (HPLC) | Cool to 4°C, Store in the dark, neutralize $Cl_2$ | 7 days[f] |
| PESTICIDES | | | | |
| Aldrin | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| *Alpha*-BHC ( -hexachlorocyclohexane) | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| *beta*-BHC ( -hexachlorocyclohexane) | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| *Delta*-BHC ( -hexachlorocyclohexane) | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| *Gamma*-BHC ( -hexachlorocyclohexane, Lindane) | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Chlordane | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| 4,4'-DDT | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| 4,4'-DDE | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| 4,4'-DDD | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Dieldrin | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| *Alpha*-Endosulfan | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| *beta*-Endosulfan | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |

| Parameter | Sample Type[a] | Recommended Analytical Test Methods[b] | Preservation[c] | Maximum Holding Time[c] |
|---|---|---|---|---|
| Endosulfan sulfate | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Endrin | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Endrin aldehyde | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Heptachlor | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Heptachlor epoxide | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Toxaphene | 24-hr. comp. | SW-846 8081A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Chlorpyrifos | 24-hr. comp. | SW-846 8141A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Parathion, (ethyl) | 24-hr. comp. | SW-846 8141A | Cool to 4°C, pH 5-9 | 7 days[f] |
| Parathion, (methyl) | 24-hr. comp. | SW-846 8141A | Cool to 4°C, pH 5-9 | 7 days[f] |
| PCB-1016 | 24-hr. comp. | SW-846 8082 | Cool to 4°C | 7 days[f] |
| PCB-1221 | 24-hr. comp. | SW-846 8082 | Cool to 4°C | 7 days[f] |
| PCB-1232 | 24-hr. comp. | SW-846 8082 | Cool to 4°C | 7 days[f] |
| PCB-1242 | 24-hr. comp. | SW-846 8082 | Cool to 4°C | 7 days[f] |
| PCB-1248 | 24-hr. comp. | SW-846 8082 | Cool to 4°C | 7 days[f] |
| PCB-1254 | 24-hr. comp. | SW-846 8082 | Cool to 4°C | 7 days[f] |
| PCB-1260 | 24-hr. comp. | SW-846 8082 | Cool to 4°C | 7 days[f] |
| DIOXINS AND FURANS<br>All dioxin and furan congeners including 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-Tetrachloro-dibenzofuran (TCDF) | 24-hr. comp. | EPA 1613 [g] | Cool to 4°C, neutralize $Cl_2$ | 7 days[f] |

## Notes on Table 1:

[a] Grab sample means a single sample taken at one moment of time or a combination of several smaller samples of equal volume taken in less than a 2 minute period. Where the term is used in connection with monitoring temperature or pH it means a single measurement.

24 hour composite sample means a combination of individual samples taken at intervals of not more than one hour such that the volumes of each of the individual samples and of the combination are proportional to the volumes of flow during each interval and during the 24 hour period respectively.

[b] Each method recommendation assumes a commonly achievable sensitivity and the strictest regulatory level. If the recommended method, or one which is comparably sensitive, is used with reasonable care, a "not detected" result is generally considered sufficient demonstration of a pollutant's absence, even if the detection limit is above the regulatory level. Any other approved method may be used for analyses if sample results are comfortably in the range of quantitation of the method or if the method's detection limit is below the regulatory level. However, if a result from a less sensitive method is reported as "not detected" and the level of detection is above the regulatory level, the Department may require the permittee to repeat the analysis using the more sensitive method. If there is no recommended method listed, any method approved in s. NR 219, Wisconsin Administrative Code may be used.

If preliminary limits are included with the permit application, the permittee, in conjunction with their lab, may use these limits to help decide if methods other that those recommended may be used (and to decide if additional sample results should be collected). If preliminary limits have not been provided for any substance, please use the recommended (or comparably sensitive) method. If a recommended method is not listed, any approved method in Chapter NR 219, Wis. Adm. Code, may be used.

For many of the most toxic of the metals, we have listed inductively coupled plasma atomic emission spectrometry (ICP) as well as graphite furnace atomic absorption spectrometry (GFAA) because many labs report ICP sensitivities that rival those of GFAA. Labs should use preliminary limits to help decide which method is most appropriate for the required sensitivity.

We have avoided recommending the older EPA metals methods from Chemical Analysis of Water and Wastes, first published in 1979 with several subsequent versions. We anticipate these methods will be de-commissioned. Instead, we have recommended the methods from Methods for the Determination of Metals in Environmental Samples, 1991 (first version). Note that, the ICP method in this more recent version, specifies use of CAL solutions with concentrations toward the lower end of the linear range.

For metals sample preparation (digestion), the older methods distinguished between "total" and "total recoverable" metals, while the newer versions drop the total designation. While the older definitions and methods are still listed in NR 219, we wish to move to the convention of only

using the total recoverable designation and urge use of the total recoverable digestion detailed in method 200.2 from Methods for the Determination of Metals in Environmental Samples.

[c] See NR 219, Table F and associated footnotes for further details on sample preservation and holding times.

[d] Standard Methods 3113B may be substituted for EPA's AA furnace method.

[e] NR 106.145 requires that permittees perform field blanks and other data quality steps. We strongly recommend that any permittee that uses surface water as its water supply source performs side-by-side intake or background surface water monitoring whenever performing effluent testing for mercury.

At this time, the following list of laboratories are certified or registered to perform the low-level mercury testing. Method 1631 is performance-based (permittees and labs may use alternative procedures so long as those procedures are demonstrated to yield reliable results at the levels of interest). The Department recognizes the capabilities of these labs to perform this low-level work because they have documented use of appropriate quality control steps for the level of sensitivity stated. The Department has asked these labs to prepare special sampling instructions aimed at minimizing sample contamination for this low-level work.

Facility sampling personnel should closely follow the instructions provided by their lab.

Commercial Labs

Battelle Marine Sciences, Sequim, Washington (Telephone (360) 683-4151).
Brooks-Rand, Washington (Telephone (206) 632-6206)
En Chem, Inc., Madison, Wisconsin (Telephone (608)232-3300.
Frontier GeoSciences, Seattle, Washington (Telephone (206) 622-6960).
Northern Lake Service, Crandon, Wisconsin (Telephone (715) 478-2777, contact Mal Gross).
S-F Analytical, Milwaukee, Wisconsin (Telephone (414) 473-6700).

Other Recognized Labs

Green Bay Metropolitan Sewerage District, Green Bay, Wisconsin (Telephone (920) 432-4893).
Madison Metropolitan Sewerage District, Madison, Wisconsin (Telephone (608) 222-1201).
Wisconsin State Laboratory of Hygiene, Madison, Wisconsin (Telephone (800) 442-4618).
Vulcan Chemicals (registered), Port Edwards, Wisconsin (Telephone (715)887-4541.
Wisconsin Electric Power Company, Milwaukee, Wisconsin (Telephone (414)221-2345.

[f] The holding time is 7 days prior to extraction, 40 days after extraction.

[g] EPA Method 1613 or Appendix C in the 5 Mill Study (EPA 440/1-88-025), March 1988.

## MONITORING PROCEDURES GUIDANCE

***A generalized procedure for obtaining chemical specific monitoring data follows. Use it to tailor your own procedure.***

A. Review specific requirements of permit or application request.

B. Hire a certified laboratory. Supply your laboratory with appropriate parts of your permit application, including the Effluent Monitoring Form, preliminary limits, if included in the application package, and associated instructions.

C. Decide when to sample.

1. Industrial discharges should be at normal to maximum levels, usually this means mid-week but avoid always sampling on the same day(s) of the week.
2. The treatment plant should be operating normally.
3. If unusual circumstances occur just before or during sampling, stop and start over after the situation has stabilized.
4. Consider sample holding times and lab workload when scheduling sampling events. Consult your laboratory prior to initiating sampling to make sure that the dates you select do not conflict with the laboratory's scheduling.
5. Consider sample transportation and laboratory arrival times.

D. Determine proper sample location.

1. The proper location is the plant effluent after all unit processes.
2. Chlorination/dechlorination processes may affect samples for various substances. Keep this in mind if disinfection processes are in operation when sampling is performed. For example, if you need to sample for cyanide amenable to chlorination and you chlorinate seasonally, collect the grab sample prior to chlorination. Also, as indicated in Table 1, the presence of chlorine also affects sample preservation requirements for certain substances.
3. The effluent stream should be well mixed at the point of sampling.

E. Prepare for sampling.

1. Obtain sample containers and proper preservation chemicals. (These items should be obtained from your laboratory.)
2. Prepare equipment; clean sampler(s). If using an automatic sampler, adhere to sampler cleaning requirements given below. For "flow through" samplers, careful cleaning and acclimation to the wastewater may be appropriate.
3. Coordinate routine testing to help serve as a measure of plant performance.
4. Contact your laboratory again to make sure they are ready for your samples.

F. Collect samples.

1. Grab samples -- Collect according to precautions and preserve. (If doing composite sampling for other parameters, the grab samples should be taken during the composite sampling.)
2. Composite sampling: NR 218 requires that composite samples be **flow-proportional**

G. Ship samples to a certified laboratory (most laboratory chain of custody forms should contain this information).

1. Ship with ice or refrigeration to maintain 4$^{o}$C. If ice packs are used or if ice is not in direct contact with the sample containers, include a 250 ml. or larger temperature blank with the samples.
2. Make sure all sample containers are clearly marked with contents, including preservatives.
3. Enclose information regarding the exact date(s) and time(s) of sampling.
4. Remember sample holding time limits.

H. When data comes back from the laboratory, report data to the Department.

1. Check data for errors. Does it look reasonable?
2. Assemble all information, including remarks on sampling and analysis.
3. Fill in all blanks on the Effluent Data Reporting Form(s)

***Cleaning Automatic Samplers***

Special provisions should be considered if using automatic samplers to collect composite samples for priority pollutant analysis. The following cleaning procedures have been suggested for suction/tubing type samplers. Alternately, consider replacing tubing and cleaning before use.

A. Pump Tubing and Line Hose Cleaning

1. Rinse by pumping hot water through the tubing for at least 2 minutes.
2. Acid rinse the tubing by pumping 20 percent hydrochloric acid or 20 percent nitric acid through the tubing for at least 2 minutes. The acid rinse should be recirculated. The acid rinse may be reused up to 4 times.
3. Repeat Step 1.
4. Rinse by pumping distilled water through the hose for at least 1 minute. After 1 minute, stop the pump and allow water to stand in the hose for at least 1 minute. After 1 minute, continue pumping rinse water for 1 additional minute. The distilled rinse should not be recirculated.
5. For priority pollutants (organics and trace metals), the hose should be flushed with pesticide grade or redistilled acetone, then rinsed again with distilled water. (Note: hose must be Teflon for organics).
6. Beware of possible zinc contamination with silicon pump tubing.

B. Sampler Cleaning - General Washing

1. Flush assembled sampler (manual or automatic) with tap water.
2. Disassemble, submerge and/or rigorously scrub all parts, which contact the sample with hot tap water and a non-phosphorus detergent.
3. Rinse and drain all items three times with tap water, and then follow with three distilled water rinses.

NOTE: Sampler bottles can be glass or polyethylene for metals, but only glass for organics. Use glass sampler bottles if sampling for metals and organics simultaneously.